

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11)

EP 1 111 031 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

27.06.2001 Bulletin 2001/26

(51) Int. Cl. 7:

C11D 3/20, C11D 1/02

(21) Application number: 99870275.7

(22) Date of filing: 22.12.1999

(84) Designated Contracting States:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE

Designated Extension States:

AL LT LV MK RO SI

(71) Applicant: THE PROCTER & GAMBLE COMPANY
Cincinnati, Ohio 45202 (US)

(72) Inventors:

, Clarke, Joanna Margaret
1000 Brussels (BE)

, Lamb, Christopher (NMN)
1380 Ohain (BE)

, Kaniecki, Marjorie Christina
1853 Strombeek-Bever (BE)

(74) Representative:

Morelle, Evelyne Charlotte Isabelle et al
BVBA Procter & Gamble Europe Sprl,
Temselaan 100
1853 Strombeek-Bever (BE)

(54) cleaning composition

(57) The present invention relates to a cleaning composition suitable for cleaning dishware. The composition comprises an anionic surfactant, preferably branched and a linear or cyclic carboxylic acid or salt thereof, such that where the acid/salt is linear it comprises from 1 to 6 carbon atoms and where the acid is cyclic it comprises greater than 3 carbon atoms.

EP 1 111 031 A1

Description

TECHNICAL FIELD

[0001] The present invention relates to a cleaning composition suitable for use in dishwashing. The dishwashing composition provides improved soil removal and especially greasy soil removal without negatively impacting the feel of the product on the surface of the dishware or the users hands, when rinsing.

BACKGROUND

[0002] Hand dishwashing composition are well known in the art. They may come in the form of pastes, gels, block, but most commonly in the form of a liquid. Such products are generally formulated to provide a number of widely diverse performance and aesthetics properties and characteristics. The majority of the cleaning performance is generally provided by surfactants that will provide acceptable solubilization and removal of food soils, especially greasy soils, from dishware being cleaned with, or in aqueous solutions formed from such products. However there is a continuing effort by formulators of liquid dishwashing compositions to incorporate additional components into dishwashing detergents to provide consumers with improved cleaning benefits.

[0003] The Applicants have found that while improving the cleaning performance of the dishwashing composition, rinse feel is also affected. By "rinse feel" it is meant the feel of the hands/dishware when composition is applied thereto, and especially when rinsing the dishware with water. The Applicants have found that whilst the formulator can improve dishwashing performance, especially on greasy soils, by including anionic surfactants the consequence of such formulation is the slipperiness of the dishes.

[0004] It is therefore an object of the present invention to improve the rinse feel of the users hands and dishware and prevent or at least reduce the slipperiness feeling provided by the dishwashing detergent composition. This objective has been met by the invention described herein

SUMMARY OF THE INVENTION

[0005] According to the present invention there is provided a cleaning composition having a pH of above 7 and comprising an anionic surfactant having from 0 to 5 mols of alkoxyl groups and a linear or cyclic carboxylic acid or salt thereof, such that where the acid/salt is linear it comprises from 1 to 6 carbon atoms and where the acid is cyclic it comprises greater than 3 carbon atoms.

[0006] In a further aspect of the present invention there is also provided a process for cleaning dishware comprising contacting the dishware with a composition as described in the preceding sentence.

[0007] In yet a further aspect of the present invention there is provided the use of an anionic surfactant comprising on average greater than 30% branching and from 0 to 5 mols of alkoxy group to provide improved rinse feel. Also provided herein is the use of a linear or cyclic carboxylic acid or salt thereof, such that where the acid/salt is linear it comprises from 1 to 6 carbon atoms and where the acid is cyclic it comprises greater than 3 carbon atoms to provide improved rinse feel.

DETAILED DESCRIPTION OF THE INVENTION

[0008] The present invention relates to a dishwashing composition. The composition may be in any suitable form, but is preferably in gel, paste and most preferably liquid form. The composition of the present invention has a pH as measured in a 10% solution thereof, of above 6. More preferably the composition has a pH of greater and 7, most preferably between 8 and 10.

[0009] In order to maintain the pH at the optimum level it may be preferably to include a buffering agent capable of providing a generally more alkaline pH in the composition and in dilute solutions. Dishwashing compositions of the present invention may therefore contain from 0.1% to 15%, preferably from 1% to 10%, most preferably from 2% to 8%, by weight, of a buffering agent. The pKa value of this buffering agent should be about 0.5 to 1.0 pH units below the desired pH value of the composition (determined as described above). Preferably, the pKa of the buffering agent should be greater than 5.

[0010] Preferred inorganic buffers/alkalinity sources include the alkali metal carbonates, alkali metal hydroxides and alkali metal phosphates, e.g., sodium carbonate, sodium hydroxide, sodium polyphosphate.

[0011] The buffering agent may be an active detergent in its own right, or it may be a low molecular weight, organic or inorganic material that is used in this composition solely for maintaining an alkaline pH. Preferred buffering agents for compositions of this invention are nitrogen-containing materials. Some examples are amino acids such as lysine or lower alcohol amines like mono-, di-, and tri-ethanolamine. The diamines, described in detail above,

also act as buffering agents and are preferred buffering agents. Preferred buffering system for use in the present detergent compositions include a combination of 0.5 % diamine and 2.5 % citrate and a combination of 0.5 % diamine, 0.75 % potassium carbonate and 1.75 % sodium carbonate. Other preferred nitrogen-containing buffering agents are Tri(hydroxymethyl)amino methane (HOCH₂)₃CNH₂ (TRIS), 2-amino-2-ethyl-1,3-propanediol, 2-amino-2-methyl-propanol, 2-amino-2-methyl-1,3-propanol, disodium glutamate, N-methyl diethanolamide, 1,3-diamino-propanol N,N'-tetra-methyl-1,3-diamino-2-propanol, N,N-bis(2-hydroxyethyl)glycine (bicine) and N-tris (hydroxymethyl)methyl glycine (tricine). Mixtures of any of the above are also acceptable. For additional buffers see McCutcheon's EMULSIFIERS AND DETERGENTS, North American Edition, 1997, McCutcheon Division, MC Publishing Company Kirk and WO 95/07971 both of which are incorporated herein by reference.

Anionic Surfactant

[0012] The compositions of the present invention comprise an anionic surfactant as an essential feature thereof. The anionic surfactant may be any suitable commonly available anionic surfactant comprising from 0 to 5 mols of alkoxy groups.

[0013] Suitable anionic surfactants for use in the compositions herein include water-soluble salts or acids of the formula ROSO₃M wherein R preferably is a C₆-C₂₀ linear or branched hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C₁₀-C₂₀ alkyl component, more preferably a C₁₀-C₁₄ alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation or ammonium or substituted ammonium, but preferably sodium.

[0014] Other suitable anionic surfactants for use herein are water-soluble salts or acids of the formula RO(A)_nSO₃M wherein R is an unsubstituted linear or branched C₆-C₂₀ alkyl or hydroxyalkyl group having a C₁₀-C₂₀ alkyl component, preferably a C₁₂-C₂₀ alkyl or hydroxyalkyl, more preferably C₁₂-C₁₄ alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, n is greater than zero, typically between about 0.5 and 5, more preferably between 0.5 and 2, and M is H or a cation which can be, for example, a metal cation, ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Exemplary surfactants are C₁₀-C₁₄ alkyl polyethoxylate (1.0) sulfate, C₁₀-C₁₄ polyethoxylate (1.0) sulfate, C₁₀-C₁₄ alkyl polyethoxylate (2.25) sulfate, C₁₀-C₁₄ polyethoxylate (2.25) sulfate, C₁₀-C₁₄ alkyl polyethoxylate (3.0) sulfate, C₁₀-C₁₄ polyethoxylate (3.0) sulfate, and C₁₀-C₁₄ alkyl polyethoxylate (4.0) sulfate, C₁₀-C₁₄ polyethoxylate (4.0) sulfate. In a preferred embodiment the anionic surfactant is a mixture of alkoxyated, preferably ethoxylated and non-alkoxyated sulfate surfactants. In such a preferred embodiment the preferred average degree of alkoxylation is from 0.4 to 0.8.

[0015] Other particularly suitable anionic surfactants for use herein are alkyl sulphonates including water-soluble salts or acids of the formula RSO₃M wherein R is a C₆-C₂₀ linear or branched, saturated or unsaturated alkyl group, preferably a C₁₀-C₂₀ alkyl group and more preferably a C₁₀-C₁₄ alkyl group, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperidinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like).

[0016] Suitable alkyl aryl sulphonates for use herein include water-soluble salts or acids of the formula RSO₃M wherein R is an aryl, preferably a benzyl, substituted by a C₆-C₂₀ linear or branched saturated or unsaturated alkyl group, preferably a C₁₂-C₁₆ alkyl group and more preferably a C₁₀-C₁₄ alkyl group, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium, calcium, magnesium etc) or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-ammonium and dimethyl piperidinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like).

[0017] In a further preferred embodiment the carbon chain of the anionic surfactant comprises alkyl, preferably C₁-4 alkyl branching units. The average percentage branching of the anionic surfactant is greater than 30%, more preferably from 35% to 80% and most preferably from 40% to 60%. Such average percentage of branching can be achieved by formulating the composition with one or more anionic surfactants all of which are preferably greater than 30% branched, more preferably from 35% to 80% and most preferably from 40% to 60%. Alternatively and more preferably, the composition may comprise a combination of branched anionic surfactant and linear anionic surfactant such that on average the percentage of branching of the total anionic surfactant combination is greater than 30%, more preferably from 35% to 80% and most preferably from 40% to 60%.

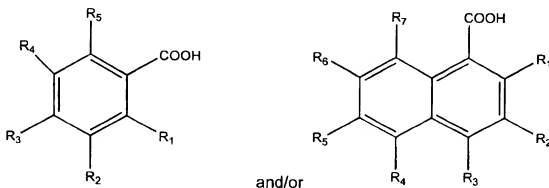
[0018] The anionic surfactant comprising on average less than 4 moles of alkoxy groups is preferably present at a level of at least 10%, more preferably from 15% to 40% and most preferably from 20% to 35% by weight of the total composition. The anionic surfactant comprising on average at least 4 moles of alkoxy groups is preferably present at a level of at least 20%, more preferably from 25% to 35% by weight of the total composition.

Carboxylic Acid

[0019] The compositions according to the present invention also comprise a linear or cyclic carboxylic acid or salt thereof. Where the acid or salt thereof is linear, it comprises from 1 to 6 carbon atoms whereas where the acid is cyclic, it comprises greater than 3 carbon atoms. The linear or cyclic carbon-containing chain of the carboxylic acid or salt thereof may be substituted with a substituent group selected from the group consisting of hydroxyl, ester, ether, aliphatic groups having from 1 to 6, more preferably 1 to 4 carbon atoms and mixtures thereof

[0020] The carboxylic acids or salts thereof preferably have a pK_{a1} of less than 7, more preferably from 1 to 3. The carboxylic acid and salts thereof may comprise one or two or more carboxylic groups.

[0021] Suitable carboxylic acids or salts thereof are those having the general formula:



wherein $R_1, R_2, R_3, R_4, R_5, R_6, R_7$ are selected from the group consisting of alkyl chain having from 1 to 3 carbon atoms, hydroxy group, hydrogen, ester group, carboxylic acid group with the proviso that no more than 3 carboxylic acid groups are present.

[0022] Preferred carboxylic acids are those selected from the group consisting of salicylic acid, maleic acid, acetyl salicylic acid, 3 methyl salicylic acid, 4 hydroxy isophthalic acid, dihydroxyfumaric acid, 1,2, 4 benzene tricarboxylic acid, pentanoic acid and salts thereof and mixtures thereof. Where the carboxylic acid exists in the salt form, the cation of the salt is preferably selected from alkali metal, alkaline earth metal, monoethanolamine, diethanolamine or triethanolamine and mixtures thereof.

[0023] The carboxylic acid or salt thereof is preferably present at the level of from 0.1 % to 5%, more preferably from 0.2% to 1% and most preferably from 0.25% to 0.5%.

[0024] As described above the compositions herein are used to provide improved rinse feel as defined below. The Applicants believe to have found that the presence of anionic surfactants, especially when present in higher amounts in the region of 15-35% by weight of the composition, results in the composition imparting a slippery feel to the hands of the user and the dishware. This feeling of slipperiness is reduced when using the compositions as defined herein i.e. the rinse feel becomes draggy. Although not wishing to be bound by theory it is the Applicants belief that the carboxylic acid provides this benefit. Moreover, it is also believed that formulating the composition with anionic surfactant, the carbon chain of which is branched such that the anionic surfactant comprises on average greater than 30% branching, can also provide or improve the rinse feel.

[0025] By the term "rinse feel" it is meant the feel of the hands of the user or the feel of the user hands on the dishware, especially when rinsing the dish with water. The type of rinse feel provided by a composition can be described as either "slippery", where it is perceived that composition and rinse water are more difficult to remove from the surface as opposed to "draggy" where it is perceived that the composition and rinse water are comparatively easier to remove. "Draggy" rinse feel can equally be detected as an increase in friction between skin of the user or between skin and dishware. By the term "improved rinse feel" it is meant herein that the compositions of the present invention provide a comparatively more "draggy" rinse feel when compared with a composition not comprising either branched anionic surfactant or carboxylic acid as defined herein or mixtures thereof.

Process of Cleaning Dishware

[0026] The present invention also relates to a process for cleaning dishware. The dishware is contacted with a composition as described above. The composition may be applied to the dishware neat or in dilute form. Thus the dishware may be cleaned singly by applying the composition to the dishware and optionally but preferably subsequently rinsing before drying. Alternatively, the composition can be mixed with water in a suitable vessel, for example a basin, sink or bowl and thus a number of dishes can be cleaned using the same composition and water (dishwater). In a further

alternative process the product can be used in dilute form in a suitable vessel as a soaking medium for, typically extremely dirty, dishware. As before the dishware can be optionally, although preferably, rinsed before allowing to dry. Drying may take place passively by allowing for the natural evaporation of water or actively using any suitable drying equipment, for example a cloth or towel.

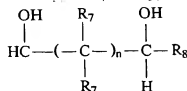
Optional Ingredients

[0027] The compositions of the present invention may also comprise optional ingredients for example diamine, additional surfactants, solvents, polymeric suds stabiliser, enzymes, builder, perfume, chelating agent and mixtures thereof.

[0028] All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified. All documents cited are, in relevant part, incorporated herein by reference.

Solvent

[0029] The present compositions may preferably comprise a solvent. Suitable solvents include diols polymeric glycols and mixtures of both diols and polymeric glycols. Diols suitable for use in the present invention have the following formula:



wherein $n = 0-3$, $\text{R}_7 = \text{H}$, methyl or ethyl, and $\text{R}_8 = \text{H}$, methyl, ethyl, propyl, isopropyl, butyl and isobutyl. Preferred diols include propylene glycol, 1,2 hexanediol, 2-ethyl-1,3-hexanediol and 2,2,4-trimethyl-1,3-pentanediol. When diols are present, the present compositions will comprise at least about 0.5 %, more preferably at least about 1%, even more preferably still, at least about 3% by weight of the composition of diols. The composition will also preferably contain no more than about 20%, more preferably no more than about 10%, even more preferably, no more than about 6% by weight of the composition of diols.

[0030] Polymeric glycols, which comprise ethylene oxide (EO) and propylene oxide (PO) groups may also be included in the present invention. These materials are formed by adding blocks of ethylene oxide moieties to the ends of polypropylene glycol chains. Polymeric glycols suitable for use in the present invention are of the following formula:



wherein $x+y$ is from about 17 to 68, and $x/(x+y)$ is from about 0.25 to 1.0. A preferred polymeric glycol is a polypropylene glycol (corresponding to when $y = 0$) having an average molecular weight of between about 1000 to about 5000, more preferably between about 2000 to about 4000, most preferably about 2000 to about 3000.

[0031] When polymeric glycols are present the present liquid detergent compositions will contain at least about 0.25 %, more preferably at least about 0.5 %, even more preferably still, at least about 0.75 % by weight of the composition of polymeric glycols. The composition will also preferably contain no more than about 5 %, more preferably no more than about 3 %, even more preferably, no more than about 2 % by weight of the composition.

[0032] To insure satisfactory physical stability, whenever polymeric glycols are added to a liquid dishwashing composition, it may be necessary to also include either a diol and/or an alkali metal inorganic salt, such as sodium chloride. Suitable amounts of diols to provide physical stability are in the amounts in the ranges found above, while a suitable amount of an alkali metal inorganic salt is at least about 0.1 % and less than about 1.5 %, preferably less than about 0.8 % by weight of the composition.

[0033] As discussed above, the addition of diols can improve the physical and enzymatic stability of a liquid dishwashing composition.

[0034] Other suitable solvents include lower alkanols, diols, other polyols, ethers, amines, and the like may be used in the present invention. Particularly preferred are the C1-C4 alkanols.

[0035] Suitable solvents for use herein include ethers and diethers having from 4 to 14 carbon atoms, preferably from 6 to 12 carbon atoms, and more preferably from 8 to 10 carbon atoms. Also other suitable solvents are glycols or alkoxylated glycols, alkoxylated aromatic alcohols, aromatic alcohols, aliphatic branched alcohols, alkoxylated aliphatic branched alcohols, alkoxylated linear C1-C5 alcohols, linear C1-C5 alcohols, C8-C14 alkyl and cycloalkyl hydrocarbons and haloalkyl hydrocarbons, C6-C16 glycol ethers and mixtures thereof.

[0036] Besides propylene glycol, polypropylene glycol and the diols illustrated above, other glycols according to the formula: HO-CR¹R²-OH wherein R¹ and R² are independently H or a C₂-C₁₀ saturated or unsaturated aliphatic hydrocarbon chain and/or cyclic are suitable and can be used herein. One such suitable glycol is dodecaneglycol.

[0037] Suitable alkoxyated glycols which can be used herein are according to the formula



wherein R is H, OH, a linear saturated or unsaturated alkyl of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, wherein R¹a is H or a linear saturated or unsaturated alkyl of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, and A is an alkoxy group preferably ethoxy, methoxy, and/or propoxy and n is from 1 to 5, preferably 1 to 2. Suitable alkoxyated glycols to be used herein are methoxy octadecanol and/or ethoxyethoxyethanol.

[0038] Suitable aromatic alcohols which can be used herein are according to the formula R-OH wherein R is an alkyl substituted or non-alkyl substituted aryl group of from 1 to 20 carbon atoms, preferably from 1 to 15 and more preferably from 1 to 10. For example a suitable aromatic alcohol to be used herein is benzyl alcohol.

[0039] Suitable aliphatic branched alcohols which can be used herein are according to the formula R-OH wherein R is a branched saturated or unsaturated alkyl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 5 to 12. Particularly suitable aliphatic branched alcohols to be used herein include 2-ethylbutanol and/or 2-methylbutanol.

[0040] Suitable alkoxyated aliphatic branched alcohols which can be used herein are according to the formula R (A) n-OH wherein R is a branched saturated or unsaturated alkyl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 5 to 12, wherein A is an alkoxy group preferably butoxy, propoxy and/or ethoxy, and n is an integer of from 1 to 5, preferably 1 to 2. Suitable alkoxyated aliphatic branched alcohols include 1-methylpropoxyethanol and/or 2-methylpropoxyethanol.

[0041] Suitable linear C₁-C₅ alcohols which can be used herein are according to the formula R-OH wherein R is a linear saturated or unsaturated alkyl group of from 1 to 5 carbon atoms, preferably from 2 to 4. Suitable linear C₁-C₅ alcohols are methanol, ethanol, propanol or mixtures thereof.

[0042] Other suitable solvents include, but are not limited to, butyl diglycol ether (BDGE), butyltriglycol ether, ter amilic alcohol and the like. Particularly preferred solvents which can be used herein are butoxy propoxy propanol, butyl diglycol ether, benzyl alcohol, butoxypropanol, ethanol, methanol, isopropanol and mixtures thereof.

[0043] Other suitable solvents for use herein include propylene glycol derivatives such as n-butoxypropanol or n-butoxypropoxypropanol, water-soluble CARBITOL R solvents or water-soluble CELLOSOLVE R solvents; water-soluble CARBITOL R solvents are compounds of the 2-(2-alkoxyethoxy)ethanol class wherein the alkoxy group is derived from ethyl, propyl or butyl; a preferred water-soluble carbitol is 2-(2-butoxyethoxy)ethanol also known as butyl carbitol. Water-soluble CELLOSOLVE R solvents are compounds of the 2-alkoxyethoxy ethanol class, with 2-butoxyethoxyethanol being preferred. Other suitable solvents include benzyl alcohol, and diols such as 2-ethyl-1, 3-hexanediol and 2,2,4-trimethyl-1,3-pentanediol and mixtures thereof. Some preferred solvents for use herein are n-butoxypropoxypropanol, BUTYL CARBITOL O and mixtures thereof.

[0044] The solvents can also be selected from the group of compounds comprising ether derivatives of mono-, di- and tri-ethylene glycol, butylene glycol ethers, and mixtures thereof. The molecular weights of these solvents are preferably less than 350, more preferably between 100 and 300, even more preferably between 115 and 250. Examples of preferred solvents include, for example, mono-ethylene glycol n-hexyl ether, mono-propylene glycol n-butyl ether, and tri-propylene glycol methyl ether. Ethylene glycol and propylene glycol ethers are commercially available from the Dow Chemical Company under the tradename "Dowanol" and from the Arco Chemical Company under the tradename "Arcosolv". Other preferred solvents including mono- and di-ethylene glycol n-hexyl ether are available from the Union Carbide company.

[0045] When present the composition will preferably contain at least about 0.01%, more preferably at least about 0.5%, even more preferably still, at least about 1% by weight of the composition of solvent. The composition will also preferably contain no more than about 20%, more preferably no more than about 10%, even more preferably, no more than about 8% by weight of the composition of solvent.

[0046] These solvents may be used in conjunction with an aqueous liquid carrier, such as water, or they may be used without any aqueous liquid carrier being present. Solvents are broadly defined as compounds that are liquid at temperatures of 20°C-25°C and which are not considered to be surfactants. One of the distinguishing features is that solvents tend to exist as discrete entities rather than as broad mixtures of compounds. Examples of suitable solvents for the present invention include ethanol, propanol, isopropanol, 2-methyl pyrrolidinone, benzyl alcohol and morpholine n-oxide. Preferred among these solvents are ethanol and isopropanol.

Diamines

[0047] Another optional although preferred ingredient of the compositions according to the present invention is a diamine. In the context of a hand dishwashing composition, the "usage levels" of such diamine in the compositions herein can vary depending not only on the type and severity of the soils and stains, but also on the wash water temperature, the volume of wash water and the length of time the dishware is contacted with the wash water.

[0048] Since the habits and practices of the users of detergent compositions show considerable variation, the composition will preferably contain at least about 0.1%, more preferably at least about 0.2%, even more preferably, at least about 0.25%, even more preferably still, at least about 0.5% by weight of said composition of diamine. The composition will also preferably contain no more than about 15%, more preferably no more than about 10%, even more preferably, no more than about 6%, even more preferably, no more than about 5%, even more preferably still, no more than about 1.5% by weight of said composition of diamine.

[0049] It is preferred that the diamines used in the present invention are substantially free from impurities. That is, by "substantially free" it is meant that the diamines are over 95% pure, i.e., preferably 97%, more preferably 99%, still more preferably 99.5%, free of impurities. Examples of impurities which may be present in commercially supplied diamines include 2-Methyl-1,3-diaminobutane and alkyldihydropyrimidine. Further, it is believed that the diamines should be free of oxidation reactants to avoid diamine degradation and ammonia formation.

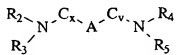
[0050] Preferred organic diamines are those in which pK1 and pK2 are in the range of about 8.0 to about 11.5, preferably in the range of about 8.4 to about 11, even more preferably from about 8.6 to about 10.75. Preferred materials for performance and supply considerations are 1,3-bis(methylamino)-cyclohexane (pKa=10 to 10.5), 1,3 propane diamine (pK1=10.5; pK2=8.8), 1,6 hexane diamine (pK1=11; pK2=10), 1,3 pentane diamine (Dytek EP) (pK1=10.5; pK2=8.9), 2-methyl 1,5 pentane diamine (Dytek A) (pK1=11.2; pK2=10.0). Other preferred materials are the primary/primary diamines with alkylene spacers ranging from C4 to C8. In general, it is believed that primary diamines are preferred over secondary and tertiary diamines.

[0051] Definition of pK1 and pK2 - As used herein, "pKa1" and "pKa2" are quantities of a type collectively known to those skilled in the art as "pKa" pKa is used herein in the same manner as is commonly known to people skilled in the art of chemistry. Values referenced herein can be obtained from literature, such as from "Critical Stability Constants: Volume 2, Amines" by Smith and Martell, Plenum Press, NY and London, 1975. Additional information on pKa's can be obtained from relevant company literature, such as information supplied by Dupont, a supplier of diamines.

[0052] As a working definition herein, the pKa of the diamines is specified in an all-aqueous solution at 25°C and for an ionic strength between 0.1 to 0.5 M. The pKa is an equilibrium constant which can change with temperature and ionic strength; thus, values reported in the literature are sometimes not in agreement depending on the measurement method and conditions. To eliminate ambiguity, the relevant conditions and/or references used for pKa's of this invention are as defined herein or in "Critical Stability Constants: Volume 2, Amines". One typical method of measurement is the potentiometric titration of the acid with sodium hydroxide and determination of the pKa by suitable methods as described and referenced in "The Chemist's Ready Reference Handbook" by Shugar and Dean, McGraw Hill, NY, 1990.

[0053] It has been determined that substituents and structural modifications that lower pK1 and pK2 to below about 8.0 are undesirable and cause losses in performance. This can include substitutions that lead to ethoxylated diamines, hydroxy ethyl substituted diamines, diamines with oxygen in the beta (and less so gamma) position to the nitrogen in the spacer group (e.g., Jeffamine EDR 148). In addition, materials based on ethylene diamine are unsuitable.

[0054] The diamines useful herein can be defined by the following structure:



wherein $R_{2,5}$ are independently selected from H, methyl, $-\text{CH}_2\text{CH}_2$, and ethylene oxides; C_x and C_y are independently selected from methylene groups or branched alkyl groups where $x+y$ is from about 3 to about 6; and A is optionally present and is selected from electron donating or withdrawing moieties chosen to adjust the diamine pKa's to the desired range, if A is present, then x and y must both be 1 or greater.

[0055] Examples of preferred diamines can be found in the copending provisional patent application of Philip Kyle Vinson et al., entitled "Dishwashing Detergent Compositions Containing Organic Diamines for Improved Grease Cleaning, Sudsing, Low Temperature Stability and Dissolution", having P & G Case No. 7167P, application serial no. 60/087,693, and filed on June 2, 1998, which is hereby incorporated by reference.

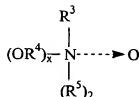
Additional surfactants

[0056] The compositions of the present invention may optionally although preferably comprise an additional surfactant. Additional surfactants may be selected from the group consisting of amphoteric, zwitterionic, nonionic other

anionic, cationic surfactants and mixtures thereof.

[0057] Amphoteric surfactants are preferred additional surfactants. The amphoteric surfactants useful in the present invention are preferably selected from amine oxide surfactants. Amine oxides are semi-polar nonionic surfactants and include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

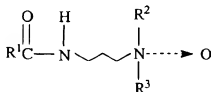
[0058] Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula



wherein R^{3a} is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R^{4a} is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R^{5a} is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R^{5a} groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

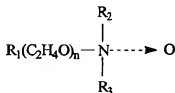
[0059] These amine oxide surfactants in particular include C_{10} - C_{18} alkyl dimethyl amine oxides and C_8 - C_{12} alkoxy ethyl dihydroxy ethyl amine oxides.

[0060] Also suitable are amine oxides such as propyl amine oxides, represented by the formula:

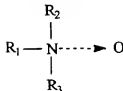


wherein R_1 is an alkyl, 2-hydroxyalkyl, 3-hydroxyalkyl, or 3-alkoxy-2-hydroxypropyl radical in which the alkyl and alkoxy, respectively, contain from about 8 to about 18 carbon atoms, R_2 and R_3 are each methyl, ethyl, propyl, isopropyl, 2-hydroxyethyl, 2-hydroxypropyl, or 3-hydroxypropyl and n is from 0 to about 10.

[0061] A further suitable species of amine oxide semi-polar surface active agents comprise compounds and mixtures of compounds having the formula:



wherein R_1 is an alkyl, 2-hydroxyalkyl, 3-hydroxyalkyl, or 3-alkoxy-2-hydroxypropyl radical in which the alkyl and alkoxy, respectively, contain from about 8 to about 18 carbon atoms, R_2 and R_3 are each methyl, ethyl, propyl, isopropyl, 2-hydroxyethyl, 2-hydroxypropyl, or 3-hydroxypropyl and n is from 0 to about 10. Particularly preferred are amine oxides of the formula:



wherein R_1 is a C_{10-14} alkyl and R_2 and R_3 are methyl or ethyl. Because they are low-foaming it may also be desirable to use long chain amine oxide surfactants which are more fully described in U.S. Pat. Nos. 4,316,824 (Pancheri), 5,075,501 and 5,071,594, incorporated herein by reference.

[0062] Other suitable, non-limiting examples of amphoteric detergent surfactants that are useful in the present invention include amido propyl betaines and derivatives of aliphatic or heterocyclic secondary and ternary amines in which the aliphatic moiety can be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to about 24 carbon atoms and at least one aliphatic substituent contains an anionic water-solubilizing group.

[0063] Further examples of suitable amphoteric surfactants are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch), hereby incorporated by reference.

[0064] Preferably the amphoteric surfactant where present, is present in the composition in an effective amount, more preferably from about 0.1% to about 20%, even more preferably about 0.1% to about 15%, even more preferably still from about 0.5% to about 10%, by weight.

[0065] Suitable nonionic detergent surfactants are generally disclosed in U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, at column 13, line 14 through column 16, line 6, incorporated herein by reference.

[0066] The condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from about 10 to about 20 carbon atoms with from about 2 to about 18 moles of ethylene oxide per mole of alcohol. Examples of commercially available nonionic surfactants of this type include Tergitol® 15-S-9 (the condensation product of $C_{11}-C_{15}$ linear secondary alcohol with 9 moles ethylene oxide), Tergitol® 24-L-6 NMW (the condensation product of $C_{12}-C_{14}$ primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol® 45-9 (the condensation product of $C_{14}-C_{15}$ linear alcohol with 9 moles of ethylene oxide), Neodol® 23-6.5 (the condensation product of $C_{12}-C_{13}$ linear alcohol with 6.5 moles of ethylene oxide), Neodol® 45-7 (the condensation product of $C_{14}-C_{15}$ linear alcohol with 7 moles of ethylene oxide), Neodol® 45-4 (the condensation product of $C_{14}-C_{15}$ linear alcohol with 4 moles of ethylene oxide), marketed by Shell Chemical Company, and Kyro® EOB (the condensation product of $C_{13}-C_{15}$ alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company. Other commercially available nonionic surfactants include Dobanol 91-8® marketed by Shell Chemical Co. and Genapol UD-080® marketed by Hoechst. This category of nonionic surfactant is referred to generally as "alkyl ethoxylates."

[0067] The preferred alkylpolyglycosides have the formula



wherein R^2a is selected from the group consisting of alkyl, alkyl-phenyl, hydroxyalkyl, hydroxyalkyl/phenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominantly the 2-position.

[0068] Fatty acid amide surfactants having the formula:



wherein R^6a is an alkyl group containing from about 7 to about 21 (preferably from about 9 to about 17) carbon atoms and each R^7a is selected from the group consisting of hydrogen, C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, and $-(C^2aH_2O)_xH$ where x varies from about 1 to about 3.

[0069] Preferred amides are C_8-C_{20} ammonia amides, monoethanolamides, diethanolamides, and isopropanolamides.

[0070] Preferably the nonionic surfactant, when present in the composition, is present in an effective amount, more preferably from about 0.1% to about 20%, even more preferably about 0.1% to about 15%, even more preferably still from about 0.5% to about 10%, by weight.

[0071] The detergent compositions hereof may also contain an effective amount of polyhydroxy fatty acid amide surfactant. By "effective amount" is meant that the formulator of the composition can select an amount of polyhydroxy fatty acid amide to be incorporated into the compositions that will improve the cleaning performance of the detergent composition. In general, for conventional levels, the incorporation of about 1%, by weight, polyhydroxy fatty acid amide will enhance cleaning performance.

[0072] Where present, the detergent compositions may comprise about 1% weight basis, polyhydroxy fatty acid amide surfactant, preferably from about 3% to about 30%, of the polyhydroxy fatty acid amide. The polyhydroxy fatty acid amide surfactant component comprises compounds of the structural formula:



wherein: R¹ is H, C₁-C₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferably C₁-C₄ alkyl, more preferably C₁ or C₂ alkyl, most preferably C₁ alkyl (i.e., methyl); and R² is a C₈-C₃₁ hydrocarbyl, preferably straight chain C₇-C₁₉ alkyl or alkenyl, more preferably straight chain C₈-C₁₇ alkyl or alkenyl, most preferably straight chain C₁₁-C₁₅ alkyl or alkenyl, or mixtures thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyethyl derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z will be a glycidyl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of -CH₂-(CHOH)_n-CH₂OH, -CH(CH₂OH)-(CHOH)_{n-1}-CH₂OH, -CH₂-(CHOH)_n-(CHOR')-(CHOH)-CH₂OH, and alkoxyethyl derivatives thereof, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide. Most preferred are glycidyls wherein n is 4, particularly -CH₂-(CHOH)₄-CH₂OH.

[0073] R' can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl.

[0074] R²a-CO-N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

[0075] Z can be 1-deoxyglucyl, 2-deoxyfructyl, 1-deoxymaltyl, 1-deoxylactyl, 1-deoxygalactyl, 1-deoxymannyl, 1-deoxymaltotriitolyl, etc.

[0076] Other additional anionic surfactants useful for deterative purposes can also be used herein. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C₈-C₂₄ olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C₈-C₂₄ alkylpolyglycol ethersulfates (containing up to 10 moles of ethylene oxide); alkyl ester sulfonates such as C₁₄₋₁₈ methyl ester sulfonates; acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C₁₂-C₁₈ monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C₈-C₁₄ diesters), sulfates of alkylpolyaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, alkyl polyethoxy carboxylates such as those of the formula RO(CH₂CH₂O)_kCH₂COO-M⁺a wherein R is a C₈-C₂₂ alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975, to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

[0077] Other particularly suitable anionic surfactants for use herein are alkyl carboxylates and alkyl alkoxy-carboxylates having from 4 to 24 carbon atoms in the alkyl chain, preferably from 8 to 18 and more preferably from 8 to 16, wherein the alkoxy is propoxy and/or ethoxy and preferably is ethoxy at an alkoxylation degree of from 0.5 to 20, preferably from 5 to 15. Preferred alkylalkoxy-carboxylate for use herein is sodium laureth 11 carboxylate (i.e.,

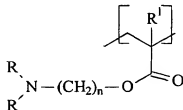
RO(C₂H₄O)₁₀-CH₂COONa, with R= C12-C14) commercially available under the name AkypoSoft® 100NV from Kao Chemical GmbH.

[0078] The particular surfactants used can therefore vary widely depending upon the particular end-use envisioned. Suitable additional surfactants are described in detail in the copending provisional patent application of Chandrika Kasturi et al., entitled "Liquid Detergent Compositions Comprising Polymeric Suds Enhancers", having P & G Case No. 6938P, application serial no. 60/066,344, incorporated above.

Polymeric Suds Stabilizer

[0079] The compositions of the present invention may optionally contain a polymeric suds stabilizer. These polymeric suds stabilizers provide extended suds volume and suds duration without sacrificing the grease cutting ability of the liquid detergent compositions. These polymeric suds stabilizers are selected from:

i) homopolymers of (N,N-dialkylamino)alkyl acrylate esters having the formula:



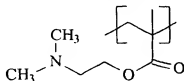
wherein each R is independently hydrogen, C₁-C₈ alkyl, and mixtures thereof, R¹ is hydrogen, C₁-C₈ alkyl, and mixtures thereof, n is from 2 to about 6; and

ii) copolymers of (i) and



wherein R¹ is hydrogen, C₁-C₆ alkyl, and mixtures thereof, provided that the ratio of (ii) to (i) is from about 2 to 1 to about 1 to 2. The molecular weight of the polymeric suds boosters, determined via conventional gel permeation chromatography, is from about 1,000 to about 2,000,000, preferably from about 5,000 to about 1,000,000, more preferably from about 10,000 to about 750,000, more preferably from about 20,000 to about 500,000, even more preferably from about 35,000 to about 200,000. The polymeric suds stabilizer can optionally be present in the form of a salt, either an inorganic or organic salt, for example the citrate, sulfate, or nitrate salt of (N,N-dimethylamino)alkyl acrylate ester.

[0080] One preferred polymeric suds stabilizer is (N,N-dimethylamino)alkyl acrylate esters, namely



[0081] When present in the compositions, the polymeric suds booster may be present in the composition from about 0.01% to about 15%, preferably from about 0.05% to about 10%, more preferably from about 0.1% to about 5%, by weight.

Builder

[0082] The compositions according to the present invention may further comprise a builder system. Because builders

such as citric acid and citrates impair the stability of enzymes in LDL compositions, it is desirable to include reduce the amounts or completely remove the builder salts normally utilized in LDL compositions incorporating propylene glycol as a builder. When a detergent composition includes propylene glycol solvent as a part or a whole of the detergent's carrier, enzymes are more stable and smaller amounts or no builder salts are needed.

[0083] If it is desirable to use a builder, then any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates and fatty acids, materials such as ethylene-diamine tetraacetate, metal ion sequestrants such as aminopolysphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylene-phosphonic acid. Though less preferred for obvious environmental reasons, phosphate builders can also be used herein.

[0084] Suitable polycarboxylates builders for use herein include citric acid, preferably in the form of a water-soluble salt, derivatives of succinic acid of the formula $R-CH_2(COOH)CH_2(COOH)$ wherein R is C_{10-20} alkyl or alkenyl, preferably C_{12-16} , or wherein R can be substituted with hydroxyl, sulfo sulfoxyl or sulfone substituents. Specific examples include lauryl succinate, myristyl succinate, palmityl succinate 2-dodecylsuccinate, 2-tetradecyl succinate. Succinate builders are preferably used in the form of their water-soluble salts, including sodium, potassium, ammonium and alkanolammonium salts.

[0085] Other suitable polycarboxylates are oxodisuccinates and mixtures of tartrate monosuccinic and tartrate disuccinic acid such as described in US 4,663,071.

[0086] Especially for the liquid execution herein, suitable fatty acid builders for use herein are saturated or unsaturated C_{10-16} fatty acids, as well as the corresponding soaps. Preferred saturated species have from 12 to 16 carbon atoms in the alkyl chain. The preferred unsaturated fatty acid is oleic acid. Other preferred builder system for liquid compositions is based on dodecyl succinic acid and citric acid.

[0087] If detergency builder salts are included, they will be included in amounts of from 0.5 % to 50 % by weight of the composition preferably from 5% to 30% and most usually from 5% to 25% by weight.

Enzymes

[0088] Detergent compositions of the present invention may further comprise one or more enzymes which provide cleaning performance benefits. Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, glucoamylases, amylases, lipases, cutinases, pectinases, xylanases, reductases, oxidases, phenoloxidases, lipoxigenases, ligninases, pullulanases, tannases, pentosanases, malanases, β -glucanases, arabinosidases or mixtures thereof. A preferred combination is a detergent composition having a cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase. Enzymes when present in the compositions, at from about 0.0001% to about 5% of active enzyme by weight of the detergent composition. Preferred proteolytic enzymes, then, are selected from the group consisting of Alcalase® (Novo Industri A/S), BPN, Protease A and Protease B (Genencor), and mixtures thereof. Protease B is most preferred. Preferred amylase enzymes include TERMAMYL®, DURAMYL® and the amylase enzymes those described in WO 9418314 to Genencor International and WO 9402597 to Novo.

[0089] Further non-limiting examples of suitable and preferred enzymes are disclosed in the copending application: "Dishwashing Detergent Compositions Containing Organic Diamines for Improved Grease Cleaning, Sudsing, Low temperature stability and Dissolution", having P & G Case No. 7167P and application serial no. 60/087,693, which is hereby incorporated by reference.

[0090] Because hydrogen peroxide and builders such as citric acid and citrates impair the stability of enzymes in LDL compositions, it is desirable to reduce or eliminate the levels of these compounds in compositions which contain enzymes. Hydrogen peroxide is often found as an impurity in surfactants and surfactant pastes. As such, the preferred level of hydrogen peroxide in the amine oxide or surfactant paste of amine oxide is 0-40 ppm, more preferably 0-15 ppm. Amine impurities in amine oxide and betaines, if present, should be minimized to the levels referred above for hydrogen peroxide.

Magnesium ions

[0091] While it is preferred that divalent ions be omitted from LDL compositions prepared according to the present invention, alternate embodiments of the present invention may include magnesium ions.

[0092] It is desirable to exclude all divalent ions from the present LDL compositions, because such ions may lead to slower dissolution as well as poor rinsing, and poor low temperature stability properties. Moreover, formulating such divalent ion-containing compositions in alkaline pH matrices may be difficult due to the incompatibility of the divalent ions, particularly magnesium, with hydroxide ions.

[0093] Nonetheless, the presence of magnesium ions offers several benefits. Notably, the inclusion of such divalent ions improves the cleaning of greasy soils for various LDL compositions, in particular compositions containing alkyl ethoxy carboxylates and/or polyhydroxy fatty acid amide. This is especially true when the compositions are used in

softened water that contains few divalent ions.

[0094] But in the present invention, these benefits can be obtained without the inclusion of divalent ions. In particular, improved grease cleaning can be achieved without divalent ions by the inclusion of organic diamines in combination with amphoteric and anionic surfactants in the specific ratios discussed above while enzymes have been shown to improve the skin mildness performance of the present LDL compositions.

[0095] If they are to be included in an alternate embodiment of the present LDL compositions, then the magnesium ions are present at an active level of from about 0.01 % to 1.5 %, preferably from about 0.015 % to 1%, more preferably from about 0.025 % to 0.5 %, by weight. The amount of magnesium ions present in compositions of the invention will be also dependent upon the amount of total surfactant present therein, including the amount of alkyl ethoxy carboxylates and polyhydroxy fatty acid amide.

[0096] Preferably, the magnesium ions are added as a hydroxide, chloride, acetate, sulfate, formate, oxide or nitrate salt to the compositions of the present invention. Because during storage, the stability of these compositions becomes poor due to the formation of hydroxide precipitates in the presence of compositions containing moderate concentrations of hydroxide ions, it may be necessary to add certain chelating agents. Suitable chelating agents are discussed further below and in U.S. Pat. No. 5,739,092, issued April 14, 1998, to Ofosu-asante, incorporated herein by reference.

Perfumes

[0097] Perfumes and perfumery ingredients useful in the present compositions and processes comprise a wide variety of natural and synthetic chemical ingredients, including, but not limited to, aldehydes, ketones, esters, and the like. Also included are various natural extracts and essences which can comprise complex mixtures of ingredients, such as orange oil, lemon oil, rose extract, lavender, musk, patchouli, balsamic essence, sandalwood oil, pine oil, cedar, and the like. Finished perfumes can comprise extremely complex mixtures of such ingredients. Finished perfumes typically comprise from about 0.01% to about 2%, by weight, of the detergent compositions herein, and individual perfumery ingredients can comprise from about 0.0001 % to about 90% of a finished perfume composition.

[0098] Non-limiting examples of perfume ingredients useful herein can be found in the copending provisional patent application: "Dishwashing Detergent Compositions Containing Organic Diamines for Improved Grease Cleaning, Sudsing, Low temperature stability and Dissolution", having P & G Case No. 7167P, application serial no. 60/087,693, incorporated above.

Chelating Agents

[0099] The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

[0100] Amino carboxylates useful as optional chelating agents include ethylenediaminetetraacetates, N-hydroxyethylthylenediaminetriacetates, nitrilo-triacetates, ethylenediamine tetrapro-pionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldi-glycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures thereof.

[0101] Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

[0102] Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

[0103] A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S, S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

[0104] The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder. Similarly, the so called "weak" builders such as citrate can also be used as chelating agents.

[0105] If utilized, these chelating agents will generally comprise from about 0.00015% to about 15% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.0003% to about 3.0% by weight of such compositions.

[0106] Other Ingredients - The detergent compositions will further preferably comprise one or more deterative

EP 1 111 031 A1

adjuncts selected from the following: soil release polymers, polymeric dispersants, polysaccharides, abrasives, bactericides and other antimicrobials, tarnish inhibitors, builders, enzymes, dyes, buffers, antifungal or mildew control agents, insect repellents, perfumes, hydrotropes, thickeners, processing aids, suds boosters, brighteners, anti-corrosive aids, stabilizers, antioxidants and chelants. A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, antioxidants, processing aids, dyes or pigments, solvents for liquid formulations, solid fillers for bar compositions, etc. If high sudsing is desired, suds boosters such as the C₁₀-C₁₈ alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C₁₀-C₁₄ monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sulfaines noted above is also advantageous.

[0107] An antioxidant can be optionally added to the detergent compositions of the present invention. They can be any conventional antioxidant used in detergent compositions, such as 2,6-di-tert-butyl-4-methylphenol (BHT), carbamate, ascorbate, thiosulfate, monoethanolamine(MEA), diethanolamine, triethanolamine, etc. It is preferred that the antioxidant, when present, be present in the composition from about 0.001% to about 5% by weight.

[0108] Various deterative ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the deterative ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the deterative ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended deterative function.

[0109] To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of C₁₃₋₁₅ ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

[0110] Further, these hand dishwashing detergent embodiments preferably further comprises a hydrotrope. Suitable hydrotropes include sodium, potassium, ammonium or water-soluble substituted ammonium salts of toluene sulfonic acid, naphthalene sulfonic acid, cumene sulfonic acid, xylene sulfonic acid.

Non-Aqueous Liquid Detergents

[0111] The manufacture of liquid detergent compositions which comprise a non-aqueous carrier medium can be prepared according to the disclosures of U.S. Patents 4,753,570; 4,767,558; 4,772,413; 4,889,652; 4,892,673; GB-A-2,158,838; GB-A-2,195,125; GB-A-2,195,649; U.S. 4,988,462; U.S. 5,266,233; EP-A-225,654 (6/16/87); EP-A-510,762 (10/28/92); EP-A-540,089 (5/5/93); EP-A-540,090 (5/5/93); U.S. 4,615,820; EP-A-565,017 (10/13/93); EP-A-030,096 (6/10/81), incorporated herein by reference. Such compositions can contain various particulate deterative ingredients stably suspended therein. Such non-aqueous compositions thus comprise a LIQUID PHASE and, optionally but preferably, a SOLID PHASE, all as described in more detail hereinafter and in the cited references.

Examples

[0112] The following examples are illustrative of the present invention, but are not meant to limit or otherwise define its scope. All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified.

	I	II	III	IV	V	VI	VII
Na C12-14E0.6S ave degree of branching 15-20%	27%	-	-	-	27%	0	0
Na C12-14E0.6S ave degree of branching 40-50%		27	20			0	0
NaC12-14E1.4S ave degree of branching 40-50%		-	-			24	25
Na C12-14E3S	-	-	-	27%	-		0

EP 1 111 031 A1

	I	II	III	IV	V	VI	VII
Amine oxide C ₁₂₋₁₄	6.5%	6.5	4	6.5%	6.5%	2	2.7
C1214 glucose amide	0	0	0	0	0	3	0
Alkyl dimethyl betaine	0	0	0	0	0	2	0
C ₁₀ E ₈	3%	3	5	3%	3%	4	0
1, 3 cyclohexane bis (methylamine)	0.5%	0.5	0	0.5%	0.5%	0	0
Homopolymer of dimethyl aminoethyl methacrylate	0.2%	0.2	0	0.2%	0.2%	0	0
Salicylic acid	0.5%	-	0.5	0.5	-	0	0.25
Maleic acid	-	-	0	-	0.5%	0.5	0.25
Ethanol	+/- 6%	7	5	+/- 6%	+/- 6%	7	7
Sodium Cumene Sulfonate	2%	4	3	4%	4%	4.5	0
NaCl	1%	1	0.6	1%	1%	0	0
Polypropylene glycol	1.5%	0	0	1.5%	1.5%	0	0.7
NaOH	balance to pH 8.4	balance to pH 8.4	balance to pH 7	balance to pH 8.4	balance to pH 8.4	balance to pH 7.8	balance to pH 7
Citric.	-	2.5	0	0	0	0	0
Mg++	0	0	0.5	0	0	0.5	0.02
C12 fatty acid	0	0	0	0	0	0	2
sodium toluene sulphonate	0	0	0	0	0	0	4
alkyl polyglucoside	0	0	0	0	0	0	2
Perfume	0.35%	0.2	0.2	0.35%	0.35%	0.2	0.12
Water	balance	balance	balance	balance	balance	balance	balance

Claims

1. A cleaning composition having a pH of above 7 and comprising an anionic surfactant having from 0 to 5 mols of alkoxy groups and a linear or cyclic carboxylic acid or salt thereof, such that where the acid/salt is linear it comprises from 1 to 6 carbon atoms and where the acid is cyclic it comprises greater than 3 carbon atoms.
2. A cleaning composition according to claim 1 wherein the composition has pH of between 8 and 10.
3. A cleaning composition according to any preceding claim wherein the anionic surfactant comprises an average carbon chain length of 6 to 20 carbon atoms.
4. A cleaning composition according to any preceding claim wherein the anionic surfactant comprises an average carbon chain length of from 10 to 14 carbon atoms.
5. A composition according to any preceding claim wherein the carbon chain of the anionic surfactant is branched.
6. A composition according to claim 5 wherein the average percentage of branching of the carbon chain of the anionic surfactant is greater than 30%, more preferably from 35% to 80% and most preferably from 40% to 60%.
7. A cleaning composition according to any preceding claim wherein the anionic surfactant comprises from 0 to 2 mols of alkoxylation.

EP 1 111 031 A1

8. A cleaning composition according to any preceding claim wherein the carboxylic acid has a pKa1 of less than 7.
9. A cleaning composition according to any preceding claim wherein the carboxylic acid has a pKa1 of from 1 to 3.
10. A cleaning composition according to any preceding claim wherein the carboxylic acid comprises one or two or more carboxylic group.
11. A cleaning composition according to any preceding claim wherein the linear or cyclic carbon-containing chain of the carboxylic acid or salt thereof is substituted with a substituent selected from the group consisting of hydroxyl, ester, ether, aliphatic groups having from 1 to 6, more preferably 1 to 4 carbon atoms and mixtures thereof
12. A cleaning composition according to any preceding claim wherein the carboxylic acid or salt thereof is selected from the group consisting of salicylic acid, maleic acid, acetyl salicylic acid, 3 methyl salicylic acid, 4 hydroxy isophthalic acid, dihydroxyfumaric acid, 1,2, 4 benzene tricarboxylic acid, pentanoic acid and salts thereof and mixtures thereof.
13. A cleaning composition according to any preceding claim wherein carboxylic acid exists in the salt form and the cation of the salt is selected from alkali metal, alkaline earth metal, monoethanolamine, diethanolamine or triethanolamine and mixtures thereof.
14. A process for cleaning dishware comprising contacting the dishware with a composition according to any of the preceding claims and optionally rinsing the dishware before or after contacting with the composition.
15. Use of an anionic surfactant comprising on average greater than 30% branching and from 0 to 5 mols of alkoxy group to provide improved rinse feel
16. Use of a linear or cyclic carboxylic acid or salt thereof, such that where the acid/salt is linear it comprises from 1 to 6 carbon atoms and where the acid is cyclic it comprises greater than 3 carbon atoms to provide improved rinse feel.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 87 0275

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 4 070 309 A (JACOBSEN RONALD LOWELL) 24 January 1978 (1978-01-24) * column 5, line 55 - column 6, line 2; claims; examples *	1-4, 7-11,13, 14	C11D3/20 C11D1/02
X	WO 94 05758 A (PROCTER & GAMBLE) 17 March 1994 (1994-03-17) * page 15, line 11 - line 18; examples *	1,3,4, 7-12	
X	EP 0 476 212 A (PROCTER & GAMBLE) 25 March 1992 (1992-03-25) * claims; examples *	1,3, 7-11,13	
X	FR 2 412 610 A (UNILEVER NV) 20 July 1979 (1979-07-20) * page 5, line 24 - page 6, line 34; claims; example 4 *	1-4, 7-11,13, 14	
X	DE 39 10 974 A (HENKEL KGAA) 11 October 1990 (1990-10-11) * page 1, line 59 - line 68; claims *	1-4, 7-11,13	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C11D
A	WO 91 16409 A (UNILEVER) 31 October 1991 (1991-10-31) * examples 1A,, 2 *	1,5-10	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 18 May 2000	Examiner Grittern, A
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document			

EPO FORM 1508/03-86 (P/02/1)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 87 0275

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

18-05-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4070309 A	24-01-1978	BE 857227 A	27-01-1978
		CA 1087478 A	14-10-1980
		DE 2733412 A	02-02-1978
		FR 2359893 A	24-02-1978
		GB 1579689 A	19-11-1980
		IT 1080759 B	16-05-1985
		JP 53049004 A	04-05-1978
		NL 7708264 A	31-01-1978
WO 9405758 A	17-03-1994	CA 2143330 A, C	17-03-1994
		CN 1086842 A	18-05-1994
		CZ 9500538 A	15-11-1995
		EP 0658188 A	21-06-1995
		JP 8500630 T	23-01-1996
		MX 9305316 A	31-01-1995
		TR 27708 A	22-06-1995
		US 5580849 A	03-12-1996
EP 0476212 A	25-03-1992	AU 8665891 A	15-04-1992
		CN 1060492 A, B	22-04-1992
		JP 6501282 T	10-02-1994
		NZ 239799 A	26-08-1994
		PT 98980 A	31-08-1992
		TR 26008 A	01-11-1993
		WO 9205238 A	02-04-1992
		US 5229028 A	20-07-1993
FR 2412610 A	20-07-1979	AT 910978 A	15-07-1981
		AU 520258 B	21-01-1982
		AU 4279578 A	28-06-1979
		BE 873051 A	22-06-1979
		BR 7808426 A	21-08-1979
		CA 1109756 A	29-09-1981
		CH 641836 A	15-03-1984
		DE 2855778 A	28-06-1979
		DK 574778 A	23-06-1979
		FI 783879 A, B,	23-06-1979
		GB 2010892 A, B,	04-07-1979
		GR 66577 A	27-03-1981
		IT 1109668 B	23-12-1985
		JP 1218063 C	17-07-1984
		JP 54099108 A	04-08-1979
		JP 58050680 B	11-11-1983
		NL 7812439 A	26-06-1979
		NO 784258 A, B,	25-06-1979
		PT 68972 A	01-01-1979

EPO FORM 900

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 87 0275

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

18-05-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 2412610 A		SE 442019 B	25-11-1985
		SE 7813213 A	23-06-1979
		ZA 7807143 A	30-07-1980
DE 3910974 A	11-10-1990	NONE	
WO 9116409 A	31-10-1991	AU 651825 B	04-08-1994
		AU 7778191 A	11-11-1991
		BR 9106381 A	27-04-1993
		CA 2080688 A,C	26-10-1991
		CN 1056707 A,B	04-12-1991
		DE 69101007 D	24-02-1994
		DE 69101007 T	05-05-1994
		EP 0526539 A	10-02-1993
		ES 2062787 T	16-12-1994
		JP 7076356 B	16-08-1995
		JP 5508427 T	25-11-1993
		KR 9513220 B	26-10-1995
		US 5672590 A	30-09-1997
		ZA 9103130 A	30-12-1992

EP FORM 1004
12/92

For more details about this annex : see Official Journal of the European Patent Office, No. 12/92

